

An Interferometric Investigation of Adsorption
by Pure Carbon from Non-Aqueous
Binary Systems Over The Entire
Concentration Range

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By
Clifford K. Sloan
1928

EASTON, PA.
MACK PRINTING CO.
1938



An Interferometric Investigation of Adsorption by Pure Carbon from Non-Aqueous Binary Systems Over The Entire Concentration Range

A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE
UNIVERSITY OF MICHIGAN

By
Clifford K. Sloan
1928

EASTON, PA.
MACK PRINTING CO.
1938

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. F. E. Bartell under whose direction this investigation was made.



CONTENTS

	Page
I. Introduction.....	5
II. Experimental Part.....	5
A. Preparation and Properties of Carbon.....	5
B. Modification of Apparatus.....	6
C. Preparation of Solutions and Method of Measurement.....	7
D. Method of Calculation of Data.....	8
E. Results of Adsorption of Solutes from Ethyl Alcohol.....	9
F. Discussion of Results.....	9
G. Measurement of Adsorption Over the Entire Concentration Range....	11
(a) System: Ethyl Alcohol-Benzene.....	11
(b) System: Ethyl Carbonate-Ethyl Alcohol.....	16
(c) System: Benzene-Ethyl Carbonate.....	17
(d) System: alpha Bromonaphthalene-Benzene.....	19
(e) System: alpha Bromonaphthalene-Ethyl Carbonate.....	21
III. Theoretical considerations.....	21
A. Application of the Gibbs Equation to Adsorption at the Carbon-Solu- tion Interface.....	21
B. Determination of Total Adsorption.....	22
C. Adsorption by Silica.....	23
IV. Summary.....	23



Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41549008_0047

AN INTERFEROMETRIC INVESTIGATION OF ADSORPTION BY PURE CARBON FROM NON-AQUEOUS BINARY SYSTEMS OVER THE ENTIRE CONCENTRATION RANGE

I. Introduction

Measurements which have been carried out for the purpose of relating the change in concentration to adsorption have, in practically all cases, been made by means of volumetric or gravimetric methods. Surprisingly few of the investigators have made use of the measurement of refractive index. In the present investigation a Rayleigh interferometer (made by Hilger) was used. Standard methods were employed for the purification of liquids.

For one who is attempting to master the technique of the interferometric method as applied to liquids the papers of Adams,³ Cohen and Bruins,⁴ and Barth and Schaum⁵ are of great value. Mitchell⁶ and Macy⁷ have recently described the use of the instrument for the measurement of the concentration of very dilute aqueous solutions. Others have found interferometry useful in adsorption problems. Odén and Anderson⁸ used the interferometer to study the adsorption of the cations of alkali and alkaline earth materials by carbon. In like manner, Ruff⁹ determined the amount of phenol adsorbed from solution by a number of commercial carbons. Oliphant and Burdon¹⁰ used the interferometer to measure adsorption of gas on mercury droplets. Others who have made use of interferometry in the study of adsorption from solution include Marc,¹¹ Wolff,¹² Arendt¹³ (who studied the velocity of adsorption by this method), Berl and Wachendorff,¹⁴ and Patrick and Jones.¹⁵

II. Experimental Part

Preparation and Properties of Carbon.—Bartell and Miller¹⁶ have

³ Adams, *J. Am. Chem. Soc.*, **37**, 481, 1181 (1915).

⁴ Cohen and Bruins, *Z. physik. Chem.*, **103**, 337 (1923).

⁵ Barth and Schaum, *Z. wiss. Phot.*, **24**, 145, 158, 166 (1926).

⁶ Mitchell, *J. Chem. Soc.*, **129**, 1333 (1926).

⁷ Macy, *J. Am. Chem. Soc.*, **49**, 3070 (1927).

⁸ Odén and Anderson, *J. Phys. Chem.*, **25**, 311 (1921).

⁹ Ruff, *Kolloid-Z.*, **38**, 59 (1926).

¹⁰ Oliphant and Burdon, *Nature*, **120**, 584 (1927).

¹¹ Marc, *Z. physik. Chem.*, **81**, 641 (1913).

¹² Wolff, *Kolloid-Z.*, **32**, 17 (1923).

¹³ Arendt, *Kolloid Chem. Beihefte*, **7**, 212 (1915).

¹⁴ Berl and Wachendorff, *Kolloid-Z.*, **36**, 36 (1925).

¹⁵ Patrick and Jones, *J. Phys. Chem.*, **29**, 1 (1925).

¹⁶ Bartell and Miller, *J. Am. Chem. Soc.*, **44**, 1866 (1922).

emphasized the importance of the use of pure carbon in adsorption experiments. They worked out a method for the activation of charcoal prepared by the carbonization of recrystallized sugar. This method, with but slight modification, was used for the preparation of a pure active carbon. The activity of the carbon was tested according to directions given by Miller.¹⁷ It was found that a quarter of a gram of carbon was capable of removing 54% of the benzoic acid from 100 cc. of a 0.02 *N* solution during ten minutes of intermittent shaking. Miller states that a fairly active carbon will adsorb 50% of the benzoic acid under these conditions. It is possible to prepare a more active carbon but this involves a greater loss in carbon due to oxidation. For the present work it was thought advisable to limit the activation treatment to four hours. A sufficiently active carbon can be obtained during that period without too greatly cutting down the yield. One hundred grams of Merck's saccharose will give about twelve grams of char. Heating this char in nitrogen at 900° reduces the amount to nine grams. The four-hour intermittent activation leaves about five grams of active carbon. After a sufficient quantity is obtained, it should be heated to drive off adsorbed moisture and then kept in a desiccator. It was found that the carbon which had been used for the adsorption of volatile organic liquids can be recovered without changing its adsorptive capacity appreciably.

Modification of Apparatus.—Activated carbon was added to different aqueous solutions of such substances as pyridine, aniline, benzene and a number of acids and alcohols. After a small amount of activated carbon had been added to a saturated solution of benzene in water, the interferometer indicated that all of the benzene had been adsorbed. In each of the other cases a pronounced adsorption of solute occurred. Because of the very slight solubility of many of these substances in water, it was thought desirable to study adsorption from a non-aqueous solvent. The interferometer, however, cannot be used without modification for the analysis of such solutions since organic liquids usually have a higher volatility, a higher temperature coefficient of refractivity and a lower heat capacity than water. Unless certain precautions are taken, these factors result in distortion of the interference band system and uncertainty in the instrument reading. Cohen and Bruins⁴ found it necessary to keep their interferometer (Zeiss type) in a water thermostat. A brass plug was made to fill all of the space above the liquid in their interferometer cell in order to prevent evaporation and distillation of liquid against the cover plate of the cell. A few attempts at measuring the concentration of non-aqueous solutions made evident the necessity of considering the precautions given by Cohen and Bruins. The compartments of the cell (Fig. 1) of the Hilger interferometer at first were covered with a plane glass plate. In many cases liquid filled the space between the cell and its cover even though great care was taken in filling the compartments. This liquid slowly evaporated. After the entire instrument had been placed in the large air thermostat used for temperature regulation, loss of liquid due to evaporation was still more pronounced because of the greater circulation of air around the cell. A steel cover was designed to fit over the top of the cell, permitting a mercury seal between the glass of the cell and the cover (Figs. 1 and 2). The under side of the latter carries a groove one-sixteenth of an inch wide extending

¹⁷ Miller, *J. Phys. Chem.*, **30**, 1162 (1926).

around the top of the glass cell and across the center between the two compartments. This groove is one-quarter of an inch deep and when filled with mercury serves as an effective means of preventing evaporation. A small hole at each end of the top of the cover permits filling the grooves with mercury after the cover is in place on the cell. Liquid is introduced into the compartments through two holes extending through the cover. Mercury seals around each of these holes prevent evaporation at these points.

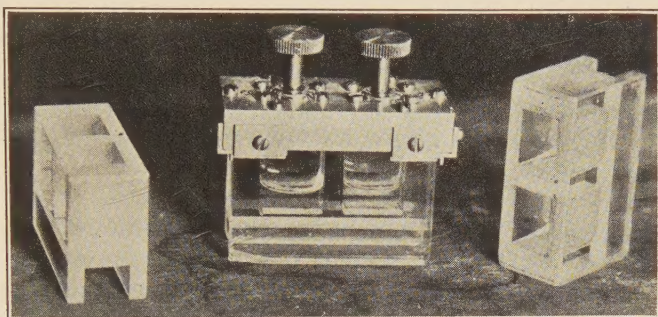


Fig. 1.

Preparation of Solutions and Method of Measurement.—All solutions were made up by weight, the most concentrated being made first and the others obtained by dilution of this with weighed amounts of solvent. The adsorption was carried out in long slender bottles with narrow necks tightly fitted with glass stoppers. The weight of carbon, m , was determined by weighing the flask before and after introduction of about a quarter of a gram of carbon. About 5 cc. of solution was then introduced and the increase in weight, N , determined. The adsorption bottles were then shaken for twenty hours and put in the air thermostat at 25° . The original solutions were also kept at this temperature for a few hours before making concentration determinations. A portion of the liquid was then removed from the carbon and compared with the original solution in the interferometer cell.

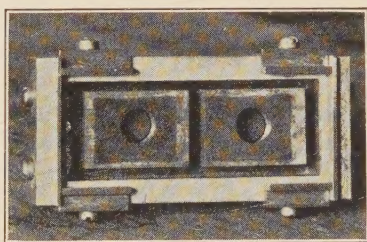


Fig. 2.

The solution of known concentration is always placed in the left-hand compartment of the cell. With this arrangement an interferometer reading greater than the zero reading indicates that the refractive index of the unknown solution is the greater. A calibration is required to determine the difference in concentration corresponding to this reading. This is made by comparing two solutions of known concentration which permits a calculation of the rate of change of concentration with instrument reading (dc/dR). It is highly desirable to compare the solution of unknown concentration with one of nearly the same concentration. If the concentration interval is too great, correction must be made for the change in appearance of the color fringes of the interference system. This phenomenon is fully discussed by Barth and Schaum.⁵ A series of calibrations in the range between zero and one per cent. of α -bromonaphthalene in alcohol shows the sensitivity of the method. One division of the interferometer is equivalent to a difference in weight concentration of 0.0000205 ($dc/dR = 0.0000205$). The concentration interval must be equivalent to less than fifty scale divi-

sions; otherwise there may be some difficulty in matching the bands correctly. In many cases adsorption is so great that the equilibrium liquid has to be compared with a solution of known concentration which differs from it less than does the original solution.

Method of Calculation of Data

The Freundlich adsorption equation has been found to apply to the adsorption of solutes when present in low concentration. The degree of adsorption from more concentrated solutions is lower than the equation would indicate. This equation states that the weight of solute removed per gram of adsorbent is proportional to a certain power of the equilibrium concentration of solute. Letting w represent the weight of solute adsorbed by m grams of adsorbent

$$w/m = a'c^n \quad (1)$$

where c represents the equilibrium concentration of solute and a' and n are constants. The measurement of the refractive index before and after adsorption gives directly the change in concentration of the solution rather than the weight of solute removed. For a small change in concentration of solute due to removal by adsorption, the change (Δc) is directly proportional both to the weight of solute removed (w) and to the concentration of solvent ($1 - c$), whereas it is inversely proportional to the total amount of solution N . We have, therefore, the relationship

$$\Delta c = a''w(1 - c)/N \quad (2)$$

Solving for w and substituting in Equation 1 gives

$$N\Delta c/(1 - c)m = ac^n \quad (3)$$

or

$$N\Delta c/m = ac^n(1 - c) \quad (4)$$

If we plot a curve from data obtained with the above equation, using $N\Delta c/m$ as one coördinate and c as the other, we find that the first portion of the curve is similar to the ordinary adsorption isotherm. The second term ($1 - c$), however, soon becomes prominent and causes the curve to pass through a maximum and then decrease to zero when c becomes unity. In this extreme case there would, of course, be no change in concentration even though a maximum of solute were adsorbed. It is evident that the change in concentration at these higher concentrations must be measured very accurately to determine whether the Freundlich equation is applicable. The measurement of refractive index with the interferometer is sufficiently accurate for this purpose.

The adsorption was first expressed in terms of $N\Delta c/m$. In order to compare the adsorption of different substances on a common basis, it was thought desirable to substitute molar units for weight units. Letting x represent the molar concentration, M_1 the gram molecular weight of solute and M_2 the gram molecular weight of solvent, we have

$$x = \frac{1}{1 + M_1(1 - c)/M_2c}$$

Letting H represent the total number of millimoles in solution and Δx the change in molar fraction due to adsorption, it can be shown that

$$H \Delta x / m = (1000x / M_2 c) (Nc / m)$$

Results of Adsorption of Solutes from Ethyl Alcohol

Some of the results obtained are given in the following tables.

TABLE I
ADSORPTION OF α -BROMONAPHTHALENE FROM ETHYL ALCOHOL^a

c_0	c	Δc	$N\Delta c/m$	x	$H\Delta x/m$
0.00400	0.00382	0.000178	0.0611	0.0000395	0.1718
.00600	.0056	.000435	.0885	.0000966	.2502
.00800	.00723	.000763	.1157	.0001696	.3255
.01000	.00863	.001367	.1377	.0003037	.3882

^a The initial and final concentrations are represented by c_0 and c_1 , respectively.

TABLE II
ADSORPTION OF BENZENE FROM ETHYL ALCOHOL

c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.01102	0.2174	0.00236	0.00866	0.0405	0.00513	0.521
.02160	.2327	.00389	.01771	.0611	.01050	0.787
.04335	.2202	.00516	.03819	.0862	.02289	1.123
.08621	.2181	.00661	.07960	.1161	.04854	1.537
.1718	.2170	.00848	.1633	.1473	.1033	2.022

TABLE III
ADSORPTION OF ETHYL CARBONATE FROM ETHYL ALCOHOL

c_0	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.00865	0.00042	0.00823	0.010	0.00323	0.084
.01765	.00073	.0170	.015	.00667	.132
.03570	.0014	.0343	.028	.0136	.24
.07178	.0018	.0700	.041	.0286	.360
.1429	.00292	.1400	.061	.0596	.566

Discussion of Results

The foregoing tables and Figure 3 indicate that the adsorption by carbon of the three solutes, α -bromonaphthalene, benzene and ethyl carbonate from ethyl alcohol is in accordance with the Freundlich equation ($H\Delta x = ax^n(1 - x)$) for the low concentrations investigated. The constants of the equations representing the adsorption of these substances from dilute alcoholic solution are given in the table below, together with the adhesion-tension¹⁸ value of each against carbon.

Solute	a	n	Adhesion tension
α -Bromonaphthalene	12.1	0.42	89.2
Benzene	9.79	.53	81.1
Ethyl carbonate	4.9	.72	65.6 ^a

^a Unpublished data.

¹⁸ Bartell and Osterhof, *Z. physik. Chem.*, **130**, 715 (1927); *Ind. Eng. Chem.*, **19**, 1277 (1927).

The order of adsorption from dilute solutions is the same as that of the adhesion tension of the solutes investigated. The coefficient, a , of the Freundlich equation increases in the same order as the adhesion-tension values, while the exponents are in the inverse order. Each of these variations corresponds to an increase in adsorption with increase in adhesion

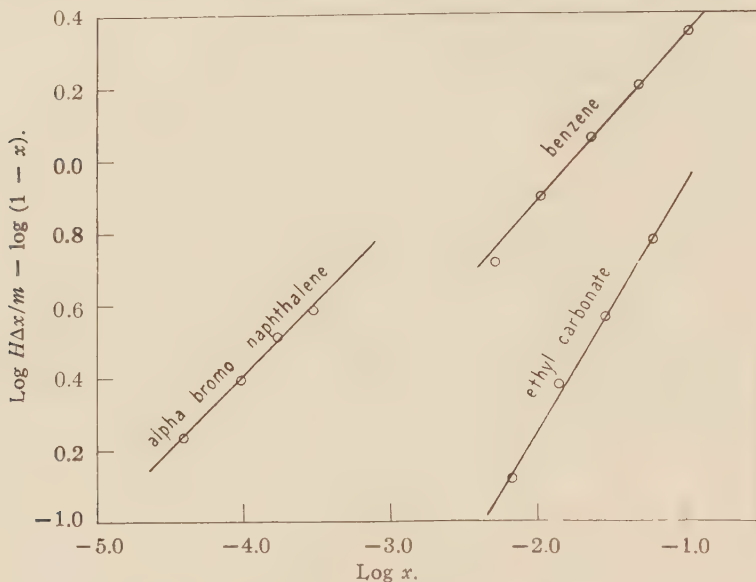


Fig. 3.—Adsorption by carbon from ethyl alcohol.

tension. Adhesion tension (A_{12}) is defined as the difference between the surface tension (S_1) of the solid and the interfacial tension (S_{12}) existing at the solid-liquid boundary.

$$A_{12} = S_1 - S_{12}$$

The adhesion tension, then, is a measure of the decrease in free surface energy which occurs when the solid-liquid interface is substituted for the solid-air interface. It is a measure of the degree to which the solid is wetted by a liquid. The Gibbs principle indicates that greatest adsorption will occur from that system which will produce the greatest lowering of interfacial tension. It may accordingly be reasoned that a liquid which is highly adsorbed by a solid will give a low interfacial tension against that solid. Furthermore, a liquid which with a given solid has a low interfacial tension will in general show a high adhesion tension with it. It is to be expected, then, disregarding solubility effects, that α -bromonaphthalene will be adsorbed to a greater extent from ethyl alcohol than will either benzene or ethyl carbonate because there will be relatively a greater decrease in the free surface energy of the system when α -bromonaphthalene comes in contact with the carbon surface.

MEASUREMENT OF ADSORPTION OVER THE ENTIRE CONCENTRATION RANGE

Adsorption from System: Ethyl Alcohol-Benzene

Since the accuracy in measurement of change in concentration by the interferometric method is practically independent of concentration, this method was used to study adsorption from non-aqueous systems over the entire concentration range. A series of dilute solutions of ethyl alcohol in benzene was prepared and adsorption by activated carbon measured.

TABLE IV
ADSORPTION OF ETHYL ALCOHOL FROM BENZENE

Init. alc. concn., $1 - c_0$	m	Δc	$1 - c$	$N\Delta c/m$	x	$H\Delta x/m$
0.01129	0.1777	0.00054	0.01075	0.0118	0.0180	0.255
.02252	.2349	.00098	.02154	.0158	.0359	.337
.04397	.1987	.00101	.04296	.0195	.0806	.412
.08137	.2575	.00067	.08070	.0099	.1294	.203
.15440	.2308	-.00048	.1549	-.0083	.2370	-.164

First, consider the adsorption of benzene when present in relatively small concentration. When the values of $\log H\Delta x/m$ are plotted against $\log x^\circ$,

a curve is obtained which is decidedly concave toward the concentration axis (Fig. 5). It has been shown that the Freundlich equation must be modified when the adsorption is measured in terms of change in concentration, the modified equation being, $H \Delta x/m = ax^n(1 - x)$.

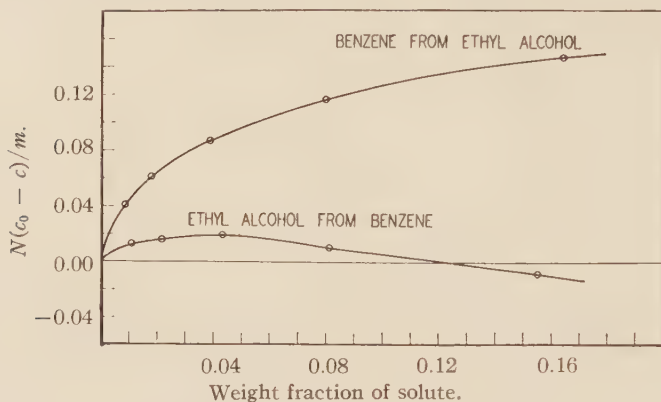


FIG. 4—Benzene from ethyl alcohol.

The plot of the difference between $\log Hx/m$ and $\log (1 - x)$ against $\log x$ should give a straight line if the adsorption of benzene follows the Freundlich equation and if no solvent is adsorbed simultaneously.

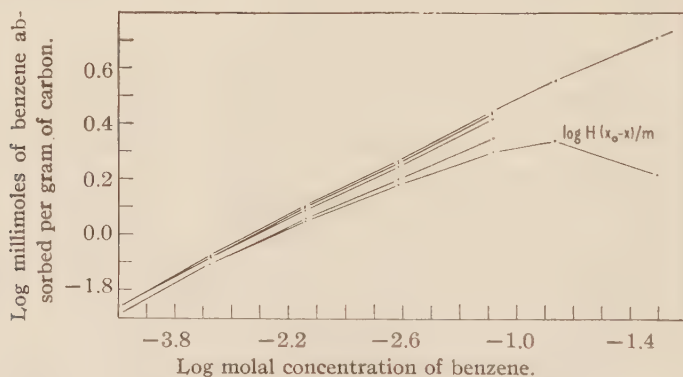


Fig. 5.—Benzene from ethyl alcohol by successive approximations.

A plot of $\log H \Delta x/m - \log (1 - x)$ against $\log x$ gives almost a straight line, though there is still a tendency to concavity toward the concentration axis. This must be due either to a decrease in the adsorption of benzene caused by the presence of ethyl alcohol, or to the fact that simultaneous adsorption of ethyl alcohol and benzene results in a smaller change in concentration than would result if benzene alone were being removed from solution.

An insight into what occurs is obtained by considering the changes in concentration resulting when carbon is added to solutions containing small amounts of ethyl alcohol. The data show that there is an adsorption of ethyl alcohol in this range. This does not mean that benzene is not taken up by the carbon. The number of molecules of benzene adsorbed at the carbon-solution interface may still greatly exceed the number of ethyl alcohol molecules adsorbed, but the fact that a lowering of concentration of alcohol results in the bulk liquid means that a higher concentration of alcohol exists in the adsorbed layer than in the bulk liquid. This process must be classed as selective adsorption of ethyl alcohol, even though actually a greater number of benzene molecules is adsorbed. The plot of $H \Delta x/m$ against the concentration of alcohol ($1 - x$) gives a curve similar

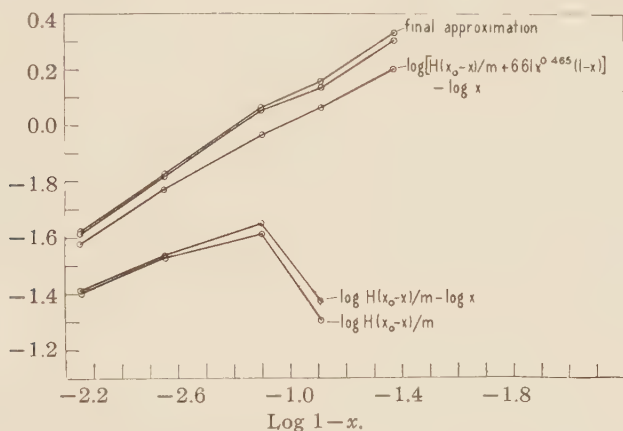


Fig. 6.—Ethyl alcohol from benzene by successive approximations.

to the curve for adsorption from very dilute solutions. The concavity of the log curve is more pronounced than that representing the adsorption of benzene from dilute solutions in ethyl alcohol. Thus, at about 0.2 mole fraction of ethyl alcohol ($x = 0.8$), carbon produces no change in the concentration of the solution (Fig. 6). There probably is pronounced adsorption at this point, but the apparent adsorption of each component is zero because the concentration of the adsorbed layer is here the same as that of the bulk liquid.

Since the apparent adsorption of each component is in accordance with the Freundlich equation when that component is present in low concentration, it is reasonable to suppose that the Freundlich equation would be applicable for the adsorption of each component over a greater concentration range. The change in concentration due to adsorption of benzene can be represented by the following equation

$$H \Delta x_1/m = ax^n(1 - x)$$

Now let us represent the change in concentration due to adsorption of ethyl alcohol by a similar equation

$$H\Delta x_2/m = b(1-x)^d$$

The resultant change in concentration will be equal to the difference between these two terms. The decrease in mole fraction of benzene resulting from the simultaneous adsorption of both components is

$$H\Delta x/m = H(x_1 - x_2)/m = ax^n(1-x) - b(1-x)^dx$$

After this formula had been derived, it was found that such an equation had been used by Wo. Ostwald⁵ to express the results of an experiment of Gustafson, who determined the adsorption from mixtures of acetic acid and phenol, concentrations being expressed in terms of weight rather than mole fraction.

Four points are necessary for the evaluation of the constants of this type of equation. The method of solution is one of successive approximations. Since the adsorption of benzene from dilute solution is governed largely by the first term of the equation, the first approximation for the constants a and n is made by plotting the difference between $\log H\Delta x/m$ and $\log (1-x)$ as a function of $\log x$. Since this plot approximates a straight line for small concentrations of benzene, two points are taken for calculation of the constants a and n , using the equation

$$\log H\Delta x/m - \log (1-x) = \log a + n \log x$$

With this approximation the change in concentration due to adsorption can be represented by the equation

$$H\Delta x/m = 6.61x^{0.465}(1-x)$$

This equation permits the calculation of the change in concentration due to benzene adsorption at those concentrations where ethyl alcohol is present in small amount. The measured adsorption of ethyl alcohol is then corrected by adding to it this calculated change in concentration due to benzene adsorption. The magnitude of the corrections is shown in Table V.

TABLE V
MAGNITUDE OF CORRECTIONS

EtOH concn.	$1-x$	0.0180	0.0359	0.0806	0.1294	0.2370
App. ads. of alc.	$-(H\Delta x/m)$	.255	.337	.412	0.203	-0.164
Benzene, ads.	$6.61x^{0.465}(1-x)$	.118	.234	.451	0.802	1.382
EtOH ads., corr.		.373	.571	.863	1.005	1.218

These corrected values are now found to be represented fairly well by the Freundlich equation. The constants b and d of the term representing the adsorption of ethyl alcohol are obtained by plotting the difference between the logarithm of the corrected value of alcohol adsorption and $\log x$ against $\log (1-x)$. This plot is much nearer a straight line than the plot obtained with uncorrected values of $H\Delta x/m$ (see Fig. 6).

⁵ Ostwald, *Kolloid-Z.*, **30**, 279 (1922); **32**, 57 (1923); **36**, 289 (1925).

The adsorption of alcohol from benzene can be represented, as a first approximation, by the equation

$$H\Delta x/m = 3.55(1-x)^{0.550}x$$

This gives a measure of the adsorption of alcohol over all ranges of concentration. The original values for the adsorption of benzene from solutions containing small amounts of benzene can now be corrected. In this case the amount of correction is much smaller, but it does, however, tend to straighten the logarithm curve (see Fig. 5).

The difference in the successive values of the constants becomes so small after a few additional approximations that the accuracy of the experimentally determined values does not warrant further approximation. The successive series of approximations representing the change in concentration due to adsorption of each component is given in Table VI. Four

TABLE VI

SUCCESSIVE SERIES OF APPROXIMATIONS			
Adsorption of benzene, $ax^n(1-x)$	Adsorption of ethyl alcohol, $b(1-x)^dx$	Adsorption of benzene, $ax^n(1-x)$	Adsorption of ethyl alcohol, $b(1-x)^dx$
$6.61x^{0.468}(1-x)$	$3.55(1-x)^{0.55}x$	$8.83x^{0.614}(1-x)$	$5.69(1-x)^{0.648}x$
$8.24x^{0.508}(1-x)$	$4.89(1-x)^{0.618}x$	$9.39x^{0.576}(1-x)$	$6.31(1-x)^{0.668}x$
$8.72x^{0.512}(1-x)$	$5.19(1-x)^{0.627}x$	$9.76x^{0.532}(1-x)$	$6.26(1-x)^{0.662}x$

additional approximations result in very little change in the values of the four constants. The decrease in concentration of benzene due to adsorption from both dilute and concentrated solutions of benzene in ethyl alcohol, therefore, is obtained by combining the last two terms of the table into a single equation.

$$H\Delta x/m = 9.76x^{0.532}(1-x) - 6.26(1-x)^{0.662}x$$

The applicability of this equation to adsorption from moderately concentrated solutions is shown by comparison with data giving adsorption of benzene at three such concentrations.

TABLE VII

ADSORPTION OF BENZENE FROM ETHYL ALCOHOL

Init. benzene concn., c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.2690	0.1682	0.00689	0.2621	0.1548	0.1725	2.213
.5268	.2366	.00612	.5207	.1026	.3907	1.672
.6854	.2193	.00343	.6820	.0573	.5586	1.019

The agreement between experimental values and those calculated by the above equations is shown in Table VIII and Fig. 7.

Adsorption from the System Ethyl Carbonate-Ethyl Alcohol.—Results of adsorption from this system are given in Table IX and Fig. 8.

TABLE VIII

ADSORPTION OF BENZENE FROM ETHYL ALCOHOL					
x	$9.76x^{0.532}(1-x)$	$6.26(1-x)^{0.662}x$	Diff.	$H\Delta x/m$	Error
0.00513	0.587	0.032	0.555	0.521	+0.034
.01050	0.855	0.065	0.790	0.787	+.003
.02289	1.280	0.141	1.139	1.123	+.016
.04854	1.857	0.294	1.563	1.537	+.026
.1033	2.616	0.602	2.014	2.022	-.008
.1725	3.173	0.953	2.220	2.213	+.007
.3907	3.608	1.761	1.847	1.672	+.175
.5586	3.160	2.034	1.126	1.019	+.107
.7630	2.004	1.841	0.163	0.164	-.001
.8706	1.174	1.406	-.232	-.203	-.029
.9194	0.756	1.097	-.341	-.412	+.071
.9641	0.344	0.667	-.323	-.337	+.014
.9820	0.174	0.430	-.256	-.255	+.001

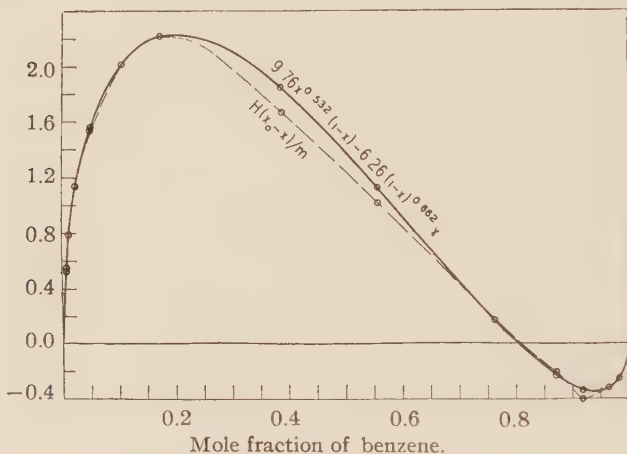


Fig. 7.—Benzene from ethyl alcohol.

TABLE IX

ADSORPTION OF ETHYL CARBONATE FROM ETHYL ALCOHOL					
c_0	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.2781	0.00326	0.2748	0.068	0.129	0.607
.5490	.00173	.5473	.038	.321	.483
.7855	-.00033	.7858	-.007	.589	-.094
.8972	-.00118	.8984	-.030	.775	-.57
.9498	-.00075	.9507	-.020	.883	-.42
.9757	-.00038	.9761	-.010	.941	-.21

The curve representing adsorption over the entire concentration range has an S-shape). Ethyl carbonate is preferentially adsorbed from solutions which are relatively dilute in ethyl carbonate; whereas ethyl

alcohol is preferentially adsorbed from solutions which are relatively dilute in alcohol. The concave nature of the logarithm curve (see Fig. 9) shows how the change in concentration due to adsorption of ethyl carbonate is influenced by the simultaneous adsorption of solvent.

The accuracy in the determination of the change in concentration due to adsorption from this system is not so great as in the other systems investi-

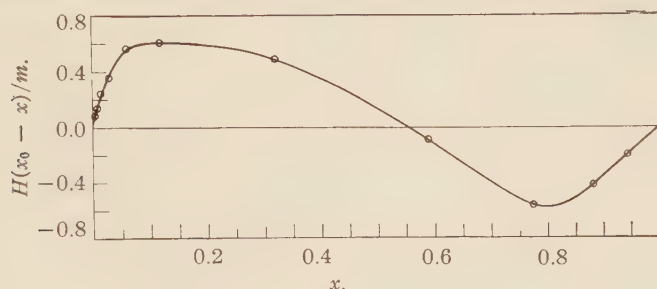


Fig. 8.—Ethyl carbonate from ethyl alcohol.

gated. This is due to the fact that there is very little difference between the refractive indices of the two components. This makes impossible an accurate calculation of the constants of the equation representing the adsorption from this system. The two parts of the S-curve are approximately the same. The exponent of the term representing the adsorption of ethyl carbonate is 0.7. The corresponding value for ethyl alcohol is 0.8.

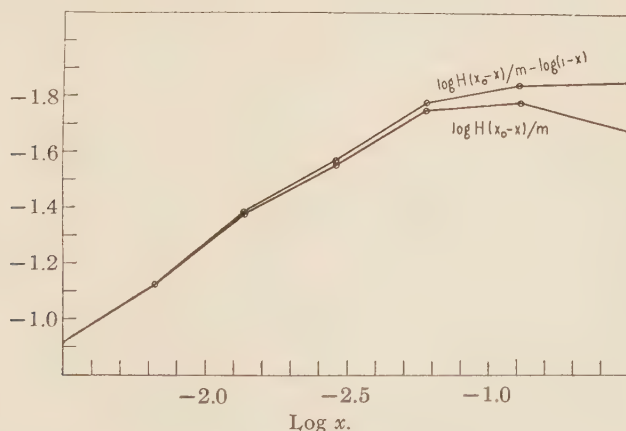


Fig. 9.—Ethyl carbonate from ethyl alcohol.

Adsorption from the System Benzene-Ethyl Carbonate.—The results of adsorption from this system are probably more striking than are those from other systems investigated. The adsorption of one of the components, benzene, conforms to the Freundlich equation up to a very high concentration of that component. This is shown by the fact that the plot

(Fig. 11) of the difference between the logarithms of $H \Delta x/m$ and x against $\log x$ is practically a straight line until x becomes 0.9. As the concentration of benzene is increased further, its adsorption is less than that indicated by the adsorption isotherm. At a molar concentration of 0.995, benzene is even slightly "negatively adsorbed." This statement does not mean that

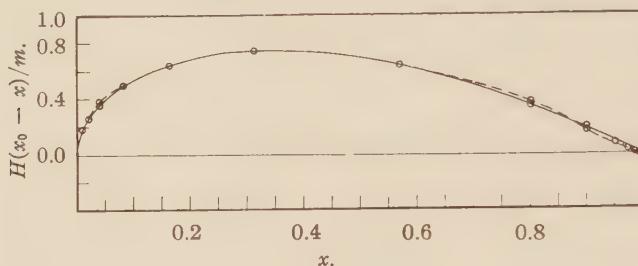


Fig. 10.—Benzene from ethyl carbonate.

benzene is not adsorbed at this concentration. There is reason to believe that the adsorption of benzene is even greater at this concentration than it is when it is *positively adsorbed* at a lower concentration. The customary use of the term, *negative adsorption*, is an unfortunate one. A reader unacquainted with the accepted meaning of this term is led to believe that the

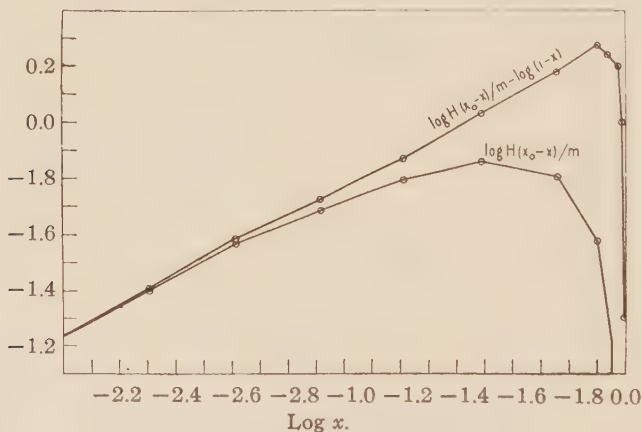


Fig. 11.—Benzene from ethyl carbonate.

other component (ethyl carbonate in this case) makes up the adsorbed layer exclusively. It would be better to speak of this as a *preferential adsorption* of ethyl carbonate rather than a *negative adsorption* of benzene. In this system the agreement of the experimentally determined points with the Freundlich equation indicates that the adsorption of ethyl carbonate is comparatively small. The straight portion of the logarithm curve permits

a calculation of the constants of the equation representing the adsorption of benzene.

$$H \Delta x / m = 2.01 x^{0.535} (1 - x)$$

The agreement between the values calculated using this equation and those experimentally determined is shown in Table X.

TABLE X
ADSORPTION OF BENZENE FROM ETHYL CARBONATE

c_0	m	Δc	c	$N \Delta c / m$	x	$H \Delta x / m$	$2.01 x^{0.535} (1 - x)$	Diff.
0.00692	0.1788	0.00053	0.00639	0.0132	0.00961	0.165	0.165	0.000
.01414	.1839	.00053	.01336	.0195	.02006	.248	.243	-.005
.02853	.1811	.00116	.02737	.0290	.04081	.366	.348	-.018
.05808	.1846	.00155	.05653	.0391	.08306	.484	.486	+.002
.1169	.1838	.00211	.1148	.0515	.1640	.621	.638	+.017
.2330	.1917	.00281	.2302	.0649	.3113	.741	.741	.000
.4705	.3444	.00499	.4655	.0631	.5683	.642	.642	.000
.7295	.2111	.00209	.7274	.0403	.8014	.375	.354	-.021
.8590	.2061	.00096	.8580	.0185	.9013	.165	.188	+.023 ^a
.93055	.2042	.00045	.93010	.0086	.9526	.075	.093	+.018 ^a
.96648	.2240	.00015	.96633	.0027	.9775	.022	.045	+.023 ^a
.98406	.2321	.00002	.98404	.0003	.9894	.002	.021	+.019 ^a
.99243	.2072	-.00004	.99247	-.0007	.9950	-.007	+.010	+.017 ^a

^a Indicates small adsorption of ethyl carbonate.

Adsorption from the System α -Bromonaphthalene-Benzene.—The adsorption from this system is shown in Table XI and Figs. 12 and 13.

TABLE XI
ADSORPTION OF α -BROMONAPHTHALENE FROM BENZENE

c	0.01077	0.02401	0.04844	0.0972	0.1928	0.3570	0.6294	0.99034
$N \Delta c / m$	.0491	.0668	.0796	.0929	.0990	.0811	.0122	-.0057
x	.00409	.00919	.01883	.0390	.0826	.1732	.3903	.9748
$H \Delta x / m$	.239	.328	.396	.478	.543	.504	.097	-.022

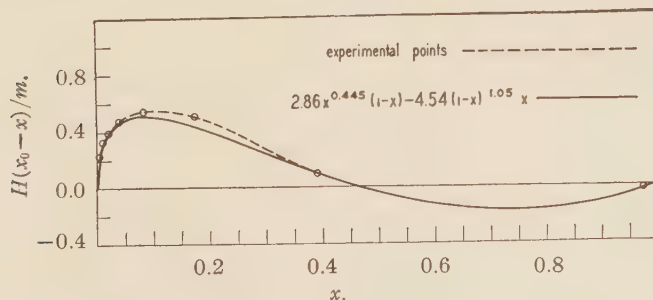


Fig. 12.— α -Bromonaphthalene from benzene.

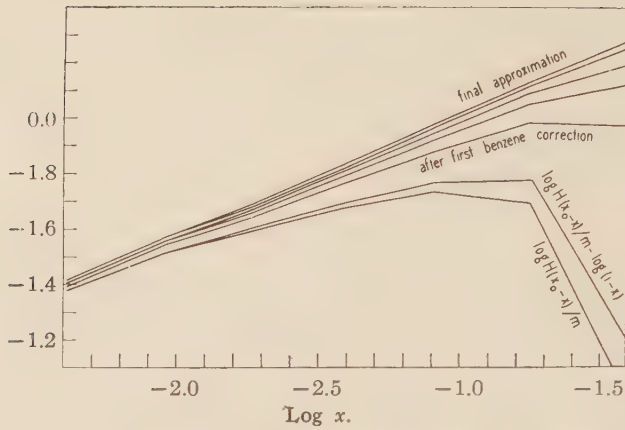


Fig. 13.—Adsorption of α -bromonaphthalene from benzene by successive approximations.

Here, again, the adsorption curve is S-shaped. The component, α -bromonaphthalene, having the higher adhesion tension against carbon is the one which is adsorbed to the greater extent. The decrease in concentration of α -bromonaphthalene due to adsorption from this system is given fairly well by the equation

$$H\Delta x/m = 2.86x^{0.445}(1-x) - 4.54(1-x)^{1.05}x$$

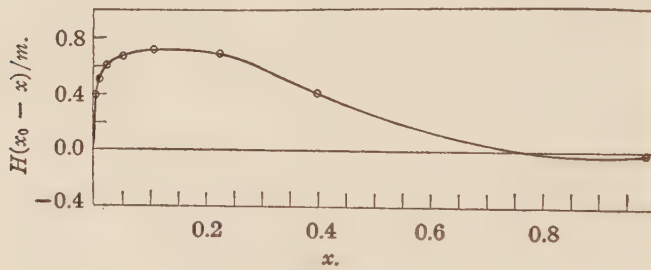


Fig. 14.— α -Bromonaphthalene from ethyl carbonate.

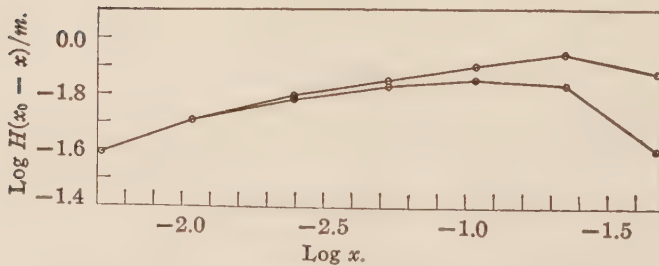


Fig. 15.— α -Bromonaphthalene from ethyl carbonate.

Adsorption from the System α -Bromonaphthalene-Ethyl Carbonate.—In this system, as in others, the adsorption of the component having the higher adhesion tension is the greater. The adsorption curve has the usual characteristics.

TABLE XII
ADSORPTION OF α -BROMONAPHTHALENE FROM ETHYL CARBONATE

c_0	m	Δc	c	$N\Delta c/m$	x	$H\Delta x/m$
0.10015	0.0860	0.00137	0.00878	0.0774	0.00519	0.388
.02124	.1339	.00290	.01834	.1009	.01091	.508
.04404	.1025	.00262	.04142	.1185	.0249	.604
.08955	.1049	.00293	.08662	.1292	.0530	.670
.1744	.1188	.00333	.1711	.1322	.1086	.711
.3327	.1369	.00318	.3295	.1183	.2262	.687
.6006	.1068	.00112	.5995	.0607	.4695	.403
.99146	.1546	— .00008	.9916	— .0034	.9871	— .025

III. Theoretical Considerations

Application of the Gibbs Equation to Adsorption at the Carbon-Solution Interface.—The results of these experiments indicate that the substance having the higher adhesion tension will be the one which will be adsorbed to the greater extent. No one component of a binary system, however, is preferentially adsorbed over the entire concentration range. From each of the systems investigated, the substance of lower adhesion tension is adsorbed if it be present in sufficiently low concentration in solution. This gives rise to the so-called S-shaped adsorption curve. This is in agreement with the work of Williams,⁶ who considered it justifiable to assume a minimum in the solid-liquid interfacial tension-concentration curve. Williams contended that the results obtained by Dora Schmidt-Walter⁷ and Gustafson⁸ indicating negative adsorption could be explained on the basis of the Gibbs adsorption equation⁹ by considering that the addition of either component to the other which is in contact with a carbon surface will result in a lowering of the interfacial tension at the carbon-liquid interface. Although there is no method for a direct measurement of these interfacial values, the existence of such minimum points is not improbable. It has been shown that, for most binary systems, the surface tension-concentration curve does have a minimum point.¹⁰ If the Gibbs adsorption formulation holds, the results of the experiments herein described point to

⁶ Williams, *Medd. Vetenskapsakad. Nobelinst.*, (2) Nr. 27 (1913) (see Freundlich, "Colloid and Capillary Chemistry," p. 179); *Proc. Roy. Soc. Edinburgh*, **37**, 161 (1916); **38**, 24 (1917); **39**, 48, 52 (1918); *Proc. Roy. Soc. London*, **96A**, 287, 298 (1920).

⁷ Schmidt-Walter, *Kolloid-Z.*, **14**, 242 (1914).

⁸ Gustafson, *Z. physik. Chem.*, **91**, 385 (1916).

⁹ Reference is here made to the rather generally used adsorption equation, $u = -(c/RT) \times dS/dc$, which has been developed from the thermodynamic rule of Gibbs relating change of concentration in the boundary layer and surface tension or interfacial tension. For lack of a better designation, this will be referred to as the Gibbs equation.

¹⁰ Freundlich, "Colloid and Capillary Chemistry," p. 53.

a more pronounced minimum point in the interfacial tensions between a solution and carbon than between a solution and air. If the method of Bartell and Osterhof¹¹ can be extended so as to measure the adhesion tension value of a binary liquid mixture against a solid, it is believed that a rigorous test can be made of the Gibbs formulation. Adhesion tension is defined by the following equation, $A_{12} = S_1 - S_{12}$. It follows that the sum of the value of the adhesion tension A_{12} and interfacial tension of a liquid against the same solid, S_{12} , must be equal to the surface tension of that solid S_1 (this latter value being constant). A change in the value of the interfacial tension with concentration at the solid-liquid interface is equal and opposite in sign to the corresponding change in adhesion tension.

$$dA_{12}/dc = -dS_{12}/dc$$

The Gibbs equation, $u = (-c/RT) \times dS_{12}/dc$, then becomes

$$u = + \frac{c}{RT} \times \frac{dA_{12}}{dc}$$

Corresponding values of dA_{12}/dc (adhesion measurements of solutions) and of u (interferometric measurement of change in concentration due to adsorption) should afford a test of the Gibbs formulation. Such a test has been lacking heretofore because no reliable data could be obtained for the values of both u and dS_{12}/dc at a single interface. This correlation should establish the importance of certain factors which are disregarded by the usual formulation of the Gibbs principle. These factors include: the change of thermodynamic potential due to adsorption of solvent as well as that of solute, electrical properties of the boundary layer and the deviation of the osmotic pressure from the ideal state.

Determination of Total Adsorption.—Williams⁶ realized that the measurement of the change in concentration gives only the apparent adsorption. He attempted, therefore, to obtain a second independent equation for the adsorption of each component by measuring the amount of each which is adsorbed by carbon from the vapor phase. The attainment of equilibrium in this latter procedure is not easy, as is shown by the recent work of Tryhorn and Wyatt¹² and Gustafson.⁸

Bakr and King,¹³ working with a benzene-iodine-carbon system, and Bakr and McBain,¹⁴ working with toluene and acetic acid, appear to have been successful in obtaining adsorption data for both solute and solvent for systems in equilibrium.

The fact that the change in concentration can be expressed quite accurately by a combination of two adsorption isotherms makes possible a cal-

¹¹ Bartell and Osterhof, *Z. physik. Chem.*, **130**, 715 (1927); *Ind. Eng. Chem.*, **19**, 1277 (1927).

¹² Tryhorn and Wyatt, *Trans. Faraday Soc.*, **21**, 399 (1927); **22**, 134, 139 (1927); **24**, 36 (1928).

¹³ Bakr and King, *J. Chem. Soc.*, **119**, 454 (1921).

¹⁴ Bakr and McBain, *J. Am. Chem. Soc.*, **46**, 2718 (1924).

ulation of the absolute adsorption of each component. If the equation $H \Delta x/m = ax^n(1-x) - b(1-x)^d x$ holds over the entire concentration range, ax^n and $b(1-x)^d$ are the respective weights of the solute and solvent adsorbed; a is the weight of solute adsorbed from pure solute. The fact that the value of a for a given solute does vary somewhat for the given solute means that the solute adsorption may be cut down to some extent by the presence of solvent. The results of Gustafson and of Bakr and McBain also indicate this. As the concentration of solute becomes large, the term $(1-x)$ decreases and the change in concentration due to solute adsorption becomes small. Even though the value of a is lower than the weight taken up from pure solute, it may still be used to represent the adsorption from the more dilute solutions.

In this investigation adsorption is expressed in terms of $H \Delta x/m$. In order to express the apparent adsorption more accurately, the change in concentration should be multiplied by the number of millimoles of solution after adsorption rather than the number before (H). Measurements indicate that as much as 5% of the solution may be adsorbed. The change in the value of H may therefore be quite appreciable unless relatively constant amounts of carbon and solution are used. A series of adsorption curves could be obtained over a limited range of concentration (about 50%) by using different amounts of carbon. If, for a given value of x , the value of $H \Delta x/m$ varies with the amount of carbon added, it will permit a calculation of the change in the value of H . This change represents the true total molecular adsorption.

Adsorption by Silica.—The measurements of Bartell and Osterhof¹¹ indicate that the order of the adhesion tension of different liquids against silica is opposite to the order against carbon. Thus benzene has a high adhesion tension against carbon, whereas the corresponding value against silica is low. On the other hand, the adhesion tension of ethyl carbonate is relatively low against carbon and high against silica. Since the adsorption from a binary system by carbon has been found to be dependent on the adhesion tension of the components against carbon, it is reasonable to expect that the adsorption by silica would be dependent on the corresponding adhesion tension values against silica. Thus, ethyl carbonate should be adsorbed by silica to a greater extent than benzene from solutions containing these two substances, inasmuch as the adhesion tension of the ethyl carbonate against silica is greater than that of benzene. This has been found to be the case. In each of the systems investigated the adsorption curve is S-shaped and the carbon and silica curves are quite opposite in nature.

Summary

The use of the interferometer in measuring the change in concentration due to adsorption from non-aqueous solutions is discussed.

Data are given for the adsorption by carbon of α -bromonaphthalene, benzene and ethyl carbonate from dilute solutions in ethyl alcohol.

It is pointed out that the adsorption of these solutes by carbon tends to be in the same order as the adhesion-tension values of these same solutes (as pure liquids) against carbon. It is probable that this relationship would obtain in all cases were it not for the influence of other factors such, for example, as solubility of solute with solvent.

The interferometric method is used to measure the adsorption by carbon from a number of binary non-aqueous systems over the entire concentration range. In each case the adsorption curve is S-shaped. The component having the higher adhesion tension against carbon is the one which is adsorbed to the greater extent. When the component of lower adhesion tension is present in very low concentration it is, however, preferentially adsorbed.

An equation

$$H\Delta x/m = ax^n(1-x) - b(1-x)^dx$$

is used to represent the preferential adsorption over the entire concentration range. The derivation of this equation is made on the assumption that the adsorption of each component follows the Freundlich equation.

It is pointed out that the adsorption at a given interface must depend on the rate of change of that particular interfacial tension with the concentration of the bounding phases. The importance of the measurement of adhesion tension values of solutions is pointed out since the rate of change of adhesion tension is equal and opposite in sign to the rate of change of interfacial tension with concentration.

The Gibbs principle is restated in terms of adhesion tension rather than interfacial tension. "*There will be an excess in the concentration of the solute in the interfacial layer if the rate of change of the adhesion tension of the solution against the adsorbent is positive.*" It is pointed out that the usual formulation of the principle of Gibbs does not take into consideration a number of existing factors. It is felt that a correlation of the data from adsorption and adhesion tension measurements will permit a more complete formulation of this principle.

